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1 TITLE: A Method, and Article of the Method, for Fabricating a
2 Flexible, Hollow Waveguide.

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4 Field of the Invention ← Center

5 Best Available Copy

6 The present invention relates to waveguides and methods
7 of making same, and more particularly to a flexible, rugged
8 waveguide comprising a photonic, bandgap, hollow fiber,
9 transmitting in the infrared and visible regions.

10 *Initial Caps.*
11 BACKGROUND OF THE INVENTION ←

12
13 The flexible waveguide of this invention is based upon
14 technology disclosed in United States Patent Nos. 5,815,627;
15 issued: September 29, 1998; 5,567,471, issued: October 22,
16 1996; and 5,440,664; issued: August 8, 1995, which technology
17 and teachings are meant to be incorporated herein by way of
18 reference. The aforementioned waveguide inventions have a
19 common inventor, James Harrington, and a common assignee,
20 Rutgers University. In aforementioned United States Patent No.
21 5,815,627, it was taught that waveguides are capable of
22 guiding both IR and visible radiation. This is also a
23 distinguishing feature of this invention. This invention,

24 however, has fabricated a waveguide that can be tailored for
25 use over a wide wavelength range by the use of multiple,
26 uniform, film coatings deposited by liquid phase chemistry
27 methods. The coatings of the inventive waveguide have an
28 additive, are fabricated by an additive technique rather than
29 a subtractive method, i.e. the former Ag layer as taught in
30 the aforementioned patents, was originally depleted in part,
31 with the establishment of the AgI layer. The AgI layer is
32 totally absent in the present application. Even the Ag layer
33 is only present in one embodiment thereof, and is but one
34 selection of other metals used for the metallic underlay.

35

36 This invention utilizes dielectric layers of sulfide
37 materials, which are built in stacked geometries to fashion
38 unique waveguide structures.

39

40 The waveguides of the present invention can be fabricated
41 in one of two novel ways:

42

43 (a) The dielectric layers of cadmium and lead
44 sulfide can be applied directly to the smooth
45 bore surface of a silica glass tube; or

46

47 (b) The dielectric layers of the cadmium and lead
48 sulfides can be applied to a metallic surface,
49 for example, metals selected from a group
50 consisting of Ag, Au, Cu, Pt, Ni, Pt, Mb, and
51 Al, which has been smoothly coated upon the
52 smooth inner bore of the silica glass tube.

54 A protective polymer coating is layered upon the outer
55 surface of the tube in both embodiments. The dielectric
56 layers of this invention comprise CdS and PbS, which form a
57 unique compatibility pair, in which deposition of each
58 material does not affect the underlying layer. These paired
59 sulfides can be stacked in multiple, thin film layers to
60 provide specific and unique characteristics. The sulfide
61 layers are deposited using similar liquid-phase chemistry
62 taught in the prior patents. The thickness of each layer can
63 be tailored for use over a wide range of wavelengths. The
64 measured losses for a single layer of CdS or a PbS film
65 deposited over an Ag layer was in agreement with the prior
66 Ag/AgI film studied at 10.6 μ m for applications using CO₂ IR
67 lasers.

69 The CdS and PbS materials have disparate refractive
70 indices with a ratio of about 2 to 1. This is often referred
71 to in this technology, as the index contrast ratio. The high
72 contrast of this layering makes possible a photonic bandgap
73 hollow fiber. The deposit of the cadmium sulfide layer
74 provides the transmission in the visible region.

75

76 Discussion of Related Art:

77

78 Prior-art hollow waveguides can provide poor beam quality
79 (poor transverse spatial coherence). ~~FIG. 12B of Gregory &~~ ^{Figure}
80 ~~(see below for) Figures~~ Harrington and ~~FIGS.~~ 5 and 6 of Croitoru et al.,
81 "Characterization of hollow fibers for the transmission of
82 infrared radiation", Appl. Opt. v. 29, 1805-1809 (20 Apr.,
83 1990) and Dror et al., "Hollow Tubes for Transmitting IR Laser
84 Energy for Surgery Applications", presented to ICALEO '89
85 (15-20 Jan., Los Angeles), are representative of the
86 characteristics of prior art hollow waveguides.

87 United States Patent Nos. 5,815,627; issued: September
88 29, 1998; 5,567,471, issued: October 22, 1996; and 5,440,664;
89 issued: August 8, 1995, depict Ag/AgI film waveguides.
90 Typically, waveguides such as are disclosed in Matsuura &
91 Miyagi, "Low-loss metallic hollow waveguides coated with

92 durable and nontoxic ZnS", Appl. Phys. Lett. v. 61, 1622-1623
93 (5 Oct., 1992) is superior. Waveguides with metal tube walls
94 that serve as the supporting structure for any coatings (such
95 as disclosed in U.S. Pat. No. 5,005,944, issued to Laakman et
96 al., and U.S. Pat. No. 4,913,505, issued to Levy '505) may be
97 capable of handling substantial power, but are semi flexible
98 at best. Those with plastic tube walls (such as disclosed in
99 U.S. Pat. No. 4,930,863, issued to Croitoru et al.) are
100 flexible, but have marginal power-handling capability at best
101 and high loss. Yet-earlier devices such as disclosed in U.S.
102 Pat. No. 3,436,141, issued to Comte, U.S. Pat. No. 3,583,786,
103 issued to Marcatili, and U.S. Pat. No. 3,963,828, issued to
104 Onoda et al., have not proven useful for the applications of
105 present interest at the wavelengths of present interest.

106

107 Hollow waveguide fibers having an index of refraction
108 less than one, have not yet attained both transmission
109 characteristics and flexibility required for many
110 applications. However, in other respects these waveguide
111 fibers are quite satisfactory at selected wavelengths. See
112 Gregory & Harrington, "Attenuation, modal, and polarization
113 properties of $n < 1$, hollow dielectric waveguides", Appl. Opt. LOK
114 v. 32, 5302-5309 (20 Sept., 1993).

115

116 As aforementioned, the current invention is an
117 improvement over the waveguide devices of the prior aforesaid
118 Harrington patents.

119

120 The present invention has made loss measurements at key
121 laser wavelengths, e.g. as a CO₂ laser waveguide. The current
122 invention provides a flexible, hollow, waveguide, and method
123 for making same. The waveguide tube meets the need for a
124 flexible, visible and IR region, laser transmission medium
125 having a relatively low loss.

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SUMMARY OF THE INVENTION

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132 In accordance with the present invention, there is
133 featured a flexible, hollow waveguide for the transmission
134 of radiation in the infrared and visible regions, and a
135 method of making same. The waveguide comprises a hollow,
136 flexible, silica-glass tube having a transparent annular
137 body defining a bore with a smooth inner bore surface. In

138 a first embodiment, a reflective, thin film, metallic
139 layer, consisting of a metal selected from a group of
140 metals consisting of: Ag, Au, Cu, Ni, Pt, Mb, Zn, and Al,
141 is coated upon the smooth inner bore surface of the silica-
142 glass tube. A single, thin film cadmium sulfide dielectric
143 layer, or a pair of thin film dielectric, cadmium and lead
144 sulfide layers respectively, are then disposed upon said
145 reflective layer. Cadmium sulfide transmits radiation in
146 both the visible and infrared region. This pair of sulfide
147 layers has disparate refractive indices with a ratio of
148 approximately 2 : 1, which is vital to provide high
149 contrast, and to fabricate a photonic, bandgap, hollow
150 waveguide tube. In a second embodiment, no metallic layer
151 is used, and the pair of thin film cadmium and lead sulfide
152 layers is multiply stacked directly upon the smooth, inner
153 bore of the silica-glass tube.

154

155 The thin films are deposited using dynamic wet chemistry,
156 and the thickness is tailored to minimize the attenuation
157 of the waveguide over specific infrared wavelengths.

158

159 It is an object of the present invention to provide ~~a~~ an
160 improved flexible, hollow waveguide.

161

162 It is another object of this invention to provide a
163 flexible, hollow waveguide comprising a photonic, bandgap
164 hollow fiber.

165

166 It is yet a further object of the current invention to
167 provide a flexible, hollow waveguide, which transmits
168 radiation in both the visible and infrared region.

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175 BRIEF DESCRIPTION OF THE DRAWINGS

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177 A complete understanding of the present invention may be
178 obtained by reference to the accompanying drawings, when
179 considered in conjunction with the subsequent detailed
180 description, in which:

181

182 FIGURE 1 depicts the growth kinetic graph of the thin
183 films deposited in the Ag coated 1,000- μ m bore waveguide;

184

185 FIGURE 2 shows the graph of the UV-VIS spectra of a
186 1,000- μ m bore Ag/CdS waveguide

187

188 FIGURE 3 illustrates the graph of the FTIR spectra of a
189 1,000- μ m bore Ag/Pbs waveguide;

190

191 FIGURE 4 depicts a graph of the cross-sectional FESEM
192 image of a 1,000- μ m bore Ag/CdS/PbS waveguide;

193

194 FIGURE 5 shows a graph of the FTIR spectra of a 1,000- μ m
195 bore of Ag/CdS and Ag/PbS, Ag/CdS/PbS and Ag/CdS/PbS/CdS
196 waveguide;

197

198 FIGURE 6 illustrates a partial schematic view of the
199 first embodiment of the waveguide of this invention;

200

201 FIGURE 6a depicts a partial schematic view of the second
202 embodiment of the waveguide of this invention;

203

204

205

205

DESCRIPTION OF THE PREFERRED EMBODIMENT

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206

207 Generally speaking, a flexible, hollow, waveguide is
208 featured, that functions in the infrared and visible regions.

209 The waveguide comprises a hollow, flexible, silica-glass tube
210 having a smooth bore that is coated in one embodiment with a
211 reflective, metal substance on the inner bore surface. A pair
212 of sulfide materials respectively of cadmium and lead sulfide,
213 is then layered over the reflective substance. The sulfide
214 materials form a high contrasting refractive index of
215 approximately 2 : 1, thus creating a photonic, bandgap tube.
216 In a second embodiment, the metallic layer is not used, and
217 the pair of sulfide layers is singularly or multiply stacked
218 directly upon the bore.

219

220 There are two embodiments of the invention. The first
221 embodiment fabricates the waveguide by liquid phase deposition
222 of a metallic, reflective layer, usually Ag upon the smooth
223 inner bore surface of the silica-glass tube. Other metals of
224 choice such as Au, Cu, Ni, Pt, Zn, Mb, Al, etc., can also be
225 used. Then, a single or pair of sulfide-containing
226 dielectrics is coated over the metal. In the second
227 embodiment of the invention, no metallic or reflective layer

228 is deposited, and only pairs of sulfide-containing dielectric
229 films are coated upon the smooth inner bore.

230

231 Now referring to ~~FIGURE~~ 6, a first embodiment of the waveguide
232 1 of this invention is illustrated. The waveguide 1,
233 comprises a silica-glass tube 3, having a thin-wall of
234 approximately 50 to 200 microns wall thickness, and a smooth
235 inner bore. A reflective, metallic layer 4 is coated over the
236 smooth bore using liquid phase chemistry, as taught in the
237 aforementioned patents. The reflective layer may comprise Ag,
238 Au, Ni, Cu, Al, Pt, Zn, Mb, etc. A single layer of cadmium
239 sulfide, or paired sulfide composite of cadmium sulfide and
240 lead sulfide, respectively, is layered over the reflective
241 layer 4. The sulfide composite comprises respective layers 5
242 and 6, of cadmium and lead sulfides. The sulfide materials
243 form a high contrast, refractive index of approximately 2 : 1
244 creating a photonic, bandgap tube. The silica-glass tube 3 is
245 covered with an outer layer 2 of plastic for protection.

246

247 Referring to FIGURE 6a, a waveguide ~~10~~ is shown having a
248 flexible, hollow, silica-glass tube ~~11~~ ³ upon which is stacked
249 at least one pair of cadmium and lead sulfide layers ~~12~~ ⁵ and
250 ~~14~~ ⁶, respectively. A multiplicity of pairs of cadmium and lead

251 sulfide layers ⁵ ~~12~~ and ⁶ ~~14~~ can be deposited over the first pair,
252 as shown in phantom.

253

254 Examples: *No Bold*

255

256 1. A smooth, inner bore surface 3 of a flexible
257 hollow tube 2 of a waveguide 1, is coated with a
258 metallic, reflective layer 4 of silver. The
259 silver layer 4 was then coated with cadmium
260 sulfide to form layer 5, and then coated with
261 lead sulfide to form layer 6. Each layer was
262 coated using liquid phase chemistry, utilizing a
263 peristaltic pump. The flow rate of the
264 solutions through the hollow tube was chosen at
265 30 ml/min.

266 The cadmium sulfide coating was applied over
267 the Ag coating, using one of the two chemical
268 baths.

269 1. I) Cadmium Nitrate 0.1 M, II) thiourea 0.5 M -
270 this is considered a full concentration
271 solution. For most depositions, the
272 concentration was reduced to 1/2 to 1/6 the
273 full concentration.

274 2. I) Cadmium acetate 5mM, II) thiourea 100mM.

275
276 All the coating solutions were prepared in
277 distilled and deionized water. The solutions are
278 prepared using an ultrasonicator or a magnetic
279 stirrer.

280 The Cd ion containing solution is complexed
281 with ammonium hydroxide solution. Initial addition
282 of ammonia will form a white precipitate of Cd(OH)₂
283 and the solution becomes turbid. With further
284 addition of ammonia dissolves the white precipitate
285 and forms a soluble Cd-ammonia complex. The solution
286 pH is maintained between 10 and 13 using sodium
287 hydroxide solution and nitric acid as titrating
288 agents. The second solution of sulfide ion is
289 prepared by dissolving thiourea in water. The two
290 solutions were then flowed through the hollow tube
291 and coated the Ag. The complexed Cd ion solution
292 reacts with the sulfide ion containing solution to
293 deposit ^a_A thin film of CdS. The hollow tube was dried
294 in flowing air.

295 2. For deposition of PbS thin films, lead nitrate was
296 used as the source of Pb ions and thiourea or a mix of

297 thiourea and thioacetamide was the source of sulfide
298 ions. All the solutions were prepared in distilled and
299 deionized water (DI). The solutions are prepared using
300 an ultrasonicator or a magnetic stirrer. The chemical
301 bath used for the deposition of lead sulfide is as
302 given below:

303 Solution 1: A) $\text{Pb}(\text{NO}_3)_2$: 4g / 500 ml; b) NaOH : 12
304 > g/500ml and

305 Solution 2: thiourea: 6g/ 1000 ml or thiourea 4g and
306 thioacetamide 2 g to 1000ml of water. <

307 The NaOH solution is slowly added to the $\text{Pb}(\text{NO}_3)_2$
308 solution while continuing to stir. Initially the
309 solution turns turbid due to the precipitation of
310 $\text{Pb}(\text{OH})_2$ which dissolves to form a soluble Na-Pb-
311 hydroxide complex on further addition of NaOH . The
312 complexed lead ion reacts with a sulfide ion in
313 solution to form PbS . Deposition of PbS requires that
314 the solutions containing Pb and S ions are
315 supersaturated in order to precipitate out in solution
316 and nucleate heterogeneously on the substrate. The
317 bore surface of the waveguide was coated with the
318 solutions using the peristaltic pump as previously
319 shown. Surfaces were air dried.

320

321 3. Infrared and visible region investigation of Ag/CdS,
322 Ag/PbS, Ag/CdS/PbS and Ag/CdS/PbS/CdS waveguides, as
323 can be observed with reference to the FIGURES 1
324 through 3 and 5, will now be described.

325

326 In the original work on omni directional waveguides authored by
327 Fink, et al. ^(insert ref. 3 into p. 26) an all-dielectric structure of alternating low/high
328 index films was described. In this invention, use of a metallic
329 film in conjunction with a multilayer dielectric stack means that
330 the waveguide will need fewer dielectric layers to achieve the same
331 loss as an all dielectric omni directional structure. CdS and PbS
332 films are transparent in the 2 to 12 μm region. The refractive
333 indices of CdS and PbS are 2.25 and 4.27 at 1.55 μm and 2.25 and
334 4.0 at 10.6 μm , respectively. This gives an index contrast of
335 $4.27/2.25 = 1.9$ at 1.55 μm and 1.78 at 10.6 μm . These two
336 dielectric materials and other sulfides such as ZnS and ZnSe may be
337 deposited in thin film form using straightforward solution
338 chemistry methods. ^(insert refs. 4+6 from p. 26) Furthermore, these two materials are
339 compatible, and the wet chemistry methods used to deposit both
340 films are similar. ^(insert refs. 7+8 from p. 26)

341

342 Dielectric-coated metallic hollow waveguides of this invention are
343 designed to minimize the attenuation of the waveguide over a
344 particular IR wavelength region by optimizing the thickness of each
345 dielectric layer. The well-established theory of Miyagi and
346 *(insert ref. 9 from pg. 27)*
347 Kawakami ¹⁰ was used to calculate the expected losses for multilayers
348 of CdS and PbS coatings. Using this theory, and the n and k values
349 for CdS and PbS, the losses for single and multilayer films at both
350 1.55 and 10.6 μm were calculated. The calculations at 10.6 μm show
351 that a 1,000- μm bore of a hollow glass waveguide with a 3-layer ^{stack}
352 ^{stack}
353 of CdS/PbS/CdS films deposited over Ag will have a straight loss of
354 0.016 dB/m compared to a straight loss of 0.07 dB/m for a single
355 layer CdS film deposited over Ag. That is, the calculated
356 attenuation coefficients are approximately four times less for the
357 three layer design, compared to a single dielectric layer at 10.6 μm ,
358
359

360 As aforementioned, hollow glass waveguides are prepared in a
361 two step process in which an Ag film is first deposited on the
362 inner surface of the silica tubing and then a dielectric layer of
363 CdS or PbS is deposited on top of the metallic layer. For
364 multilayer dielectric structures, sequential deposition of
365 alternating low/high films leads to the structures, Ag/CdS,
366 Ag/CdS/PbS, and Ag/CdS/PbS/CdS. The Ag film is deposited on the
367 inner surface of the silica tubing using a liquid-phase reduction

art

reaction typical of that used in the prior ~~patents to Harrington~~
using Ag/AgI hollow glass waveguides¹⁰⁻¹² ~~(Insert refs. 10, 12, and 14, page 27)~~. The thickness of the Ag film is chosen to be sufficiently thick to prevent any transmission through the film, but thin enough so that the surface roughness is as low as possible. Specifically, the thickness of the Ag film is chosen to be at least ten times the skin depth at 10.6 μm . The skin depth of an Ag film at 10.6 μm is 12 nm. In all the experiments CdS and PbS have been deposited on Ag films that vary in thickness from 150 to 200 nm. At this thickness the Ag films are quite smooth (< 12 nm rms roughness) and, therefore, they provide a good surface for the deposition of the dielectric layers. A very important feature of the CdS and PbS coatings is that they are additive and, thus, independent of the Ag film. This is in strong contrast to the waveguides made using AgI coatings^{13, 14} ~~(Insert refs. 11, 13, and 14, page 27)~~. AgI is deposited in a subtractive process in which AgI is formed by the diffusion of iodine ions into the underlying silver film. Therefore, to produce a thick dielectric layer of AgI will require a thick starting layer of ~~an~~ ^{they} ~~(Insert 15 nm page 28)~~ Ag. In ~~the~~ ^{an} article by Rabii and Harrington¹⁴ ~~(Insert 15 nm page 28)~~ have shown that the surface roughness of both the Ag and the AgI film increases with increasing thickness of the Ag layer.

386

387 **Additional Examples:**

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next page, No bold

388

389 As aforementioned, CdS and PbS thin films were deposited using
390 a wet chemistry deposition technique⁷. Cadmium nitrate and
391 cadmium acetate are used as the source of Cd ions; lead nitrate
392 the source of Pb ions; and thiourea, $(SC(NH_2)_2$), the source of S
393 ions. It is important to accurately control pH of these
394 solutions, since the CdS and PbS precipitates are stable only in
395 the pH range 10 to 13. ^{The} pH control and chelating is achieved
396 using an ammonia solution for CdS and sodium hydroxide for PbS.
397 Specifically, the pH for aqueous $Cd(NO_3)_2$ is maintained between 11
398 and 12. Owing to the fact that the reaction rate also changes
399 with the pH, it is necessary to calibrate the process for a given
400 pH range. The thickness of both CdS and PbS increases with
401 increasing concentration of Cd, Pb and S ions in solution and
402 with increasing deposition time. From a study of the growth
403 kinetics for both CdS and PbS thin films, it has been
404 established, that the optimal concentration and flow rate
405 conditions for uniform film deposition for tubing require lengths
406 greater than 1.5 m. The best coatings were made using $> 0.01\text{ M}$
407 solutions and pumping rates of 30 ml/min.

408

409 The multilayer dielectric structures of Ag/CdS/PbS and
410 Ag/CdS/PbS/CdS, were prepared in a manner similar to the single-

411 layer dielectric metallic waveguides. The different layers were
412 coated in a sequential manner with an intermediate drying step
413 after coating each layer. An Ag-only tube was coated with a
414 single layer of either CdS, or PbS, when the 2- and 3-layer
415 structures were being coated as an independent check on the
416 thickness for each layer.

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↓

418 Optical characterization of Ag/sulfide film Waveguides:

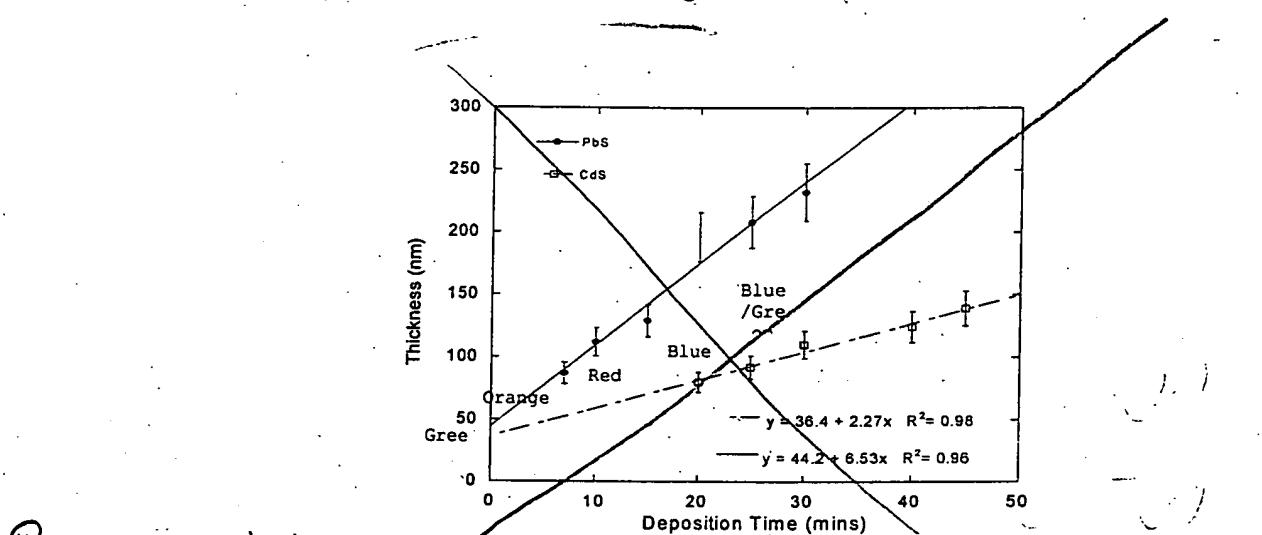
419

420 The spectral characteristics of the Ag/CdS and Ag/PbS hollow
421 glass waveguides were evaluated using a Perkin Elmer UV-VIS
422 spectrometer, and Nicolet Protégé FTIR. A typical spectral
423 response shows interference peaks, which depend on the thickness
424 of the dielectric thin films. The thickness of a single layer
425 dielectric, "d", was calculated from the peak position of the
426 longest-wavelength interference band, $\lambda_p^{(m)}$, using the relation ~~Eq.~~^{Eq. 1},

$$d = \frac{m \cdot \lambda_p^{(m)}}{4 \cdot \sqrt{n_1^2 - 1}}, \quad (1)$$

428 where m is the order of the interference maxima ($m=1$ for the
429 longest-wavelength band); λ_p is the wavelength of the m^{th}
430 absorption peak; and n_1 is the refractive index of the dielectric
431 film. From ~~Eq.~~^{Equation} (1) it is observed, that the peak position
432 shifts to longer wavelengths as the thickness of the film

433 increases. Spectral data has been used to determine the
434 thickness of films prepared using different growth kinetics. The
435 film thickness obtained from the optical measurements has then
436 been correlated with direct thickness measurements using a
437 field-emission scanning electron microscope (FESEM). In this
438 way one obtains the growth kinetic curves for CdS and PbS
439 deposited on Ag, ^{as} shown in Fig. 1. Figure 1.



441 P - In Figure 1, the
442 Fig. 1 The growth kinetic curves of the CdS and PbS thin films
443 deposited in a Ag coated, 1,000 μ m bore Hollow Glass Waveguide, are
444 show.)
445 datum points of curves 60 and 62 represent
446 regions
447 The color indicated is the color that one would see looking
448 through the waveguides with an optical microscope, microscope, and
449 are representative of film thickness.

448 All films were prepared using 0.01 M solutions and a flow rate
449 of 30 ml/min. The growth kinetics curves in Fig 1 indicate that

450 CdS (open symbols) has a slower growth rate on Ag compared to PbS
451 (solid symbols) under similar conditions. The reason for the
452 slower growth rate for CdS compared to PbS, is that the CdS
453 complexes with the ammonia used in the deposition and this
454 decreases the rate of deposition. The data also shows that the
455 thickness of both dielectrics increases linearly with time, with
456 growth rates of ~ 2.3 and 6.9 nm/min for CdS and PbS,
457 respectively. The mechanism for linear growth is based on the
458 *(Insert from p 28)* Stransi-Krastanov model of island-like growth¹⁷. This mechanism
459 involves nucleation and growth in the linear growth region. This
460 information is important as we need to carefully control film
461 thickness for single and multilayer structures. The UV-VIS
462 spectra for the Ag/CdS is given in Fig. 2, and the FTIR spectra
463 for the Ag/PbS in Fig. 3. The spectral data clearly show that the
464 position of the interference peaks^{50,51,52, and 53, respectively} shifts to longer wavelengths as
465 the thickness of the film increases as predicted by Eq. (1). It has
466 been observed relative to Figure 2.
467 also noted from the insert photos in Fig. 2, that the Hollow Glass
468 Waveguides show a color variation. This is due to selective
469 filtering of the input white light by the thin film coating
470 (interference effect). This color variation is seen with the CdS
471 coatings, but not the PbS films, because these films do not
472 transmit well at visible wavelengths.

473 The thickness of the thin films was obtained by direct
474 measurements using a FESEM. A photomicrograph taken with the
475 FESEM for a typical cross-section of the thin film combination
476 identified as 45, 46, and 47, respectively,
477 Ag/CdS/PbS is shown in Fig. 4. The CdS film appears darker than
478 the PbS film, because the in-lens detector produces a negative
479 Also, the silica substrate 44 is a portion of the tube 3,
480 nm. Degradation was not observed for the underlying film, when
481 the new film is deposited over it. That is, CdS and PbS do not
482 react with each other during the deposition of successive layers.
483 The film thickness measured from the FESEM micrographs of both
484 single and multilayer dielectric film are summarized in Table 4
485 below. These results agree very well with the optical thickness
486 measurement.

487 Table 4. Thickness values for CdS and PbS thin films on Ag
488 determined from FESEM images

HGws	Thickness of		Thickness of	
	Ag	CdS	PbS	
	nm	nm	nm	
Ag/CdS	156	172 ± 16		
Ag/PbS	158	—		96 ± 16
Ag/CdS/P	154	169		82 ± 6

489

490 A series of 1,000- μm -bore HGWs with 1, 2, and 3 dielectric layers
491 deposited over Ag were fabricated using wet chemistry methods [8,
492 11]. The spectral losses for these straight waveguides are shown
493 in ~~Fig.~~ 5. From ~~Fig.~~ 5, it may be seen that the addition of each
494 dielectric layer shifts the interference peaks to longer
wavelengths. This is a result of the increase in thickness with
each additional layer.

497

498 The thickness of each dielectric layer was determined from a ~~wi~~
499 sample composed of each dielectric layer deposited separately on ~~waveguides~~
500 ~~a slide~~. These witness samples were deposited along with the multilayer ~~waveg~~
501 From the witness samples we determined the thickness of the ~~indiv~~
502 layers using the position of the long wavelength interference peak
503 ~~from Equation~~ ~~Ex.~~ (1). The thicknesses obtained were; Ag 200 nm, CdS (adjacent to
504 ~~Ag~~) 156 nm, PbS 87 nm, and CdS (next to air) 97 nm. The thickness value
505 of CdS and PbS layers measured optically agree very well with ~~from~~ ~~FESEM~~
506 measurements and are within experimental errors as shown in Table 1.
507 ~~Figure~~ ~~Fig.~~ 5 we see that this waveguide is best suited for operation beyond
508 ~~5~~ μm .
509 ~~P~~ Losses measurements were made at 1.55 μm using a diode laser rather
510 a CO₂ laser at 10.6 μm where the HGWs would ultimately be most ~~use~~
511 The reason for using a 1.55 μm laser was that we were ~~very~~ ~~interested~~
interested in

NME

512 developing a new waveguide for secure communication systems at 1.55

513 Clearly, solid-core silica fibers are a better choice for

514 ~~most~~ applications at 1.55 μm . The output of the diode laser was ^{via}

515 ~~a~~ pigtaled single mode fiber terminated with a Selfoc lens. The ^{spectral} ~~spec~~

516 response of the HGWs chosen for loss measurements was similar to

517 ~~that~~ ^{Figure} shown in ~~Fig.~~ 5. In general, coating thicknesses were not optimized

518 ~~for~~ lowest loss at 1.55 μm ; however, as may be seen from the cut-back ^(see below) ~~measured~~

519 data given in Table 2, the losses were still quite low. The ^{meas} ~~calculated~~

520 losses in Table 2 may be compared to the theoretical losses ~~calculated~~

521 ~~at~~ both 1.55 and 10.6 μm using the n and k values of the dielectric ^(insert 9 from p. 27)

522 ~~films~~ and the theory of Miyagi and Kawakami ~~to~~. The losses at 1.55 μm are ^(K=0.39)

523 ~~high~~ when PbS is used because k is rather large at this wavelength ~~(K=0)~~.

524 At 10.6 μm k for PbS is 0.008 and the calculated loss for ~~Ag/CdS/PbS~~ ^{Ag/CdS/PbS}

525 is over four times less than for Ag/CdS. The bending losses for

526 ~~the~~ waveguides were not measured. It is well known that there is ^{which}

527 ~~an~~ additional loss on bending for non-omni directional waveguides, ^(insert 17 from p. 28)

528 varies as $1/R$, where R is the radius of the bend ~~to~~. Since

529 ~~our~~ waveguides have no more than 3 dielectric layers it is expected ^{that we} ~~the~~ ^{be}

530 would not observe omni directional behavior rather there would ~~be~~

531 ~~an~~ added loss on bending.

532 Table 2 Loss values for 1,000- μm bore HGWs with 1, 2, and 3-layer

533 dielectric coatings.

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534 ~~X~~ _____ Conclusions

	Multilayer	Measured l ₁ μm,	Theoretic 1.55 μ	Theoretic 10.6 μ	summary
536	We	Ag/CdS	0.2 ±	2.7	7.0
		Ag/PbS	0.26 :	2.5	7.3
		Ag/CdS/PbS	0.1 ±	8.6	3.3
		Ag/CdS/PbS/Cd	0.06 :	6.7	1.6

545 demonstrated that liquid-phase chemistry methods can be used to
 546 deposit good optical quality CdS and PbS thin films to form both
 547 single and multiple dielectric/metallic HGWs. The spectral response
 548 for waveguides with these films deposited over Ag show well defined
 549 interference bands indicating good film thickness uniformity over the
 550 entire length of the guide. Varying the deposition time controls the
 551 position of the interference peaks. Furthermore, we have found that
 552 CdS and PbS are compatible and the deposition of each material does
 553 not affect the underlying film. In this way the thickness of each
 554 layer in the multilayer stack can be tailored for use over a wide
 555 wavelength range. The final 3-layer stack showed that it is possible
 556 to make a multilayer coating but we have yet to reduce the
 557 attenuation to the level predicted by theory. Moreover, the measured
 558 losses for the single-layer CdS or PbS films at 1.55 μm are in
 559 general agreement with the well studied Ag/AgI HGWs at 10.6 μm (17 μm p. 28).
 560 In reality, the greatest potential for these waveguides is likely to

561 be at 10.6 μm for applications involving CO₂ laser power delivery and
562 IR fiber sensors.

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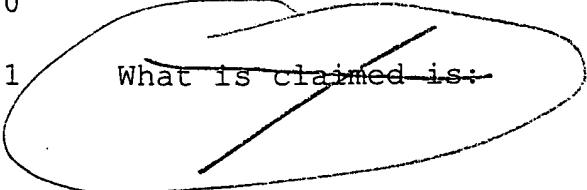
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618
619

619 ~~R~~ since other modifications and changes varied to fit
620 particular operating requirements and environments will
621 be apparent to those skilled in the art, the invention is
622 not considered limited to the example chosen for purposes
623 of disclosure and covers all changes and modifications
624 which do not constitute departures from the true spirit
625 and scope of this invention.

626
627 Having thus described the invention, what is desired to
628 be protected by Letters Patent is presented in the
629 subsequently appended claims.

630
631 
What is claimed is:

DRAWINGS

~~CdS and PbS thin films were deposited using a wet chemistry deposition technique [4]. Cadmium nitrate and cadmium acetate are used as the source of Cd ions; lead nitrate the source of Pb ions; and thiourea, $(\text{SC}(\text{NH}_2)_2$), the source of S ions. It is important to accurately control pH of these solutions since the CdS and PbS precipitates are stable only in the pH range 10 to 13. pH control and chelating is achieved using an ammonia solution for CdS and sodium hydroxide for PbS. Specifically, the pH for aqueous $\text{Cd}(\text{NO}_3)_2$ is maintained between 11 and 12. Since the reaction rate also changes with the pH, it is necessary to calibrate the process for a given pH range. The thickness of both CdS and PbS increases with increasing concentration of Cd, Pb and S ions in solution and with increasing deposition time. From a study of the growth kinetics for both CdS and PbS thin films, we have established optimal concentration and flow rate conditions for uniform film deposition for tubing with lengths greater than 1.5 m. The best coatings were made using $> 0.01 \text{ M}$ solutions and pumping rates of 30 ml/min.~~

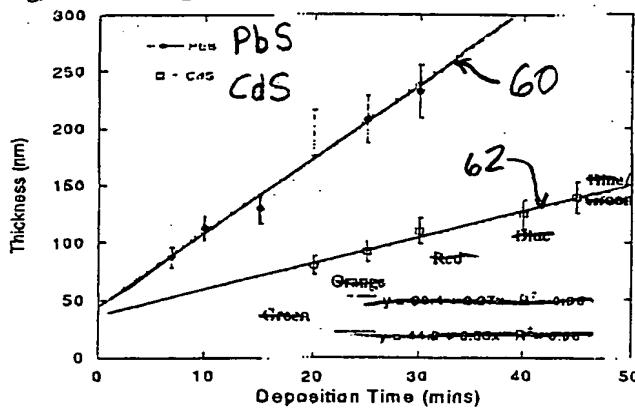
~~The multilayer dielectric structures of $\text{Ag}/\text{CdS}/\text{PbS}$ and $\text{Ag}/\text{CdS}/\text{PbS}/\text{CdS}$, were prepared in a manner similar to the single-layer dielectric metallic waveguides. The different layers were coated in a sequential manner with an intermediate drying step after coating each layer. An Ag-only tube was coated with a single layer of either CdS or PbS when the 2- and 3-layer structures were being coated as an independent check on the thickness for each layer.~~

3. Optical characterization of Ag/sulfide film HGWs

The spectral characteristics of the Ag/CdS and Ag/PbS HGWs were evaluated using a Perkin Elmer UV-VIS spectrometer and Nicolet Protégé FTIR. A typical spectral response shows interference peaks which depend on the thickness of the dielectric thin films. The thickness of a single layer dielectric, d , was calculated from the peak position of the longest-wavelength interference band, $\lambda_p^{(m)}$, using the relation [12],

$$d = \frac{m \cdot \lambda_p^{(m)}}{4 \cdot \sqrt{n_1^2 - 1}}, \quad (1)$$

where m is the order of the interference maxima ($m = 1$ for the longest-wavelength band); λ_p is the wavelength of the m^{th} absorption peak; and n_1 is the refractive index of the dielectric film. From Eq. (1) we see that the peak position shifts to longer wavelengths as the thickness of the film increases. Spectral data has been used to determine the thickness of films prepared using different growth kinetics. The film thickness obtained from the optical measurements has then been correlated with direct thickness measurements using a field-emission scanning electron microscope (FESEM). In this way we obtain the growth kinetic curves for CdS and PbS deposited on Ag, shown in Fig. 1.



~~Fig. 1. The growth kinetic curves of the CdS and PbS thin films deposited in a Ag coated, 1.000 μm bore HGW. The color indicated is the color that one would see looking through the waveguides with an optical microscope.~~

FIG. 1

~~All~~ films were prepared using 0.01 M solutions and a flow rate of 30 ml/min. The growth kinetics curves in Fig. 1 indicate that CdS (open symbols) has a slower growth rate on Ag compared to PbS (solid symbols) under similar conditions. The reason for the slower growth rate for CdS compared to PbS is that the CdS complexes with the ammonia used in the deposition and this decreases the rate of deposition. The data also show that the thickness of both dielectrics increases linearly with time, with growth rates of ~ 2.3 and 6.9 nm/min for CdS and PbS, respectively. The mechanism for linear growth is based on the Stranski-Krastanov model of island-like growth [16]. This mechanism involves nucleation and growth and we are in the linear growth region. This information is important as we need to carefully control film thickness for single and multilayer structures. The UV-VIS spectra for the Ag/CdS is given in Fig. 2 and the FTIR spectra for the Ag/PbS in Fig. 3. The spectral data clearly show that the position of the interference peaks shifts to longer wavelengths as the thickness of the film increases as predicted by Eq. (1). We also note from the insert photos in Fig. 2 that the HGWs show a color variation. This is due to selective filtering of the input white light by the thin film coating (interference effect). This color variation is seen with the CdS coatings but not the PbS films as these films do not transmit well at visible wavelengths.

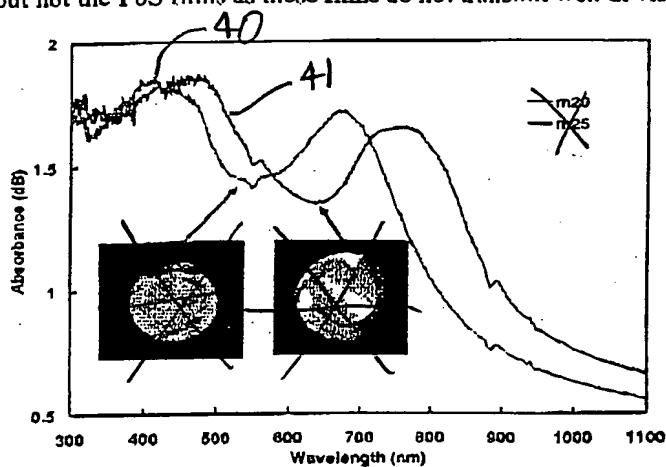


Fig. 2 UV-VIS spectra of 1,000- μm -bore Ag/CdS HGWs for different deposition times in minutes. The insert shows the color of the transmitted light as filtered by the coating.

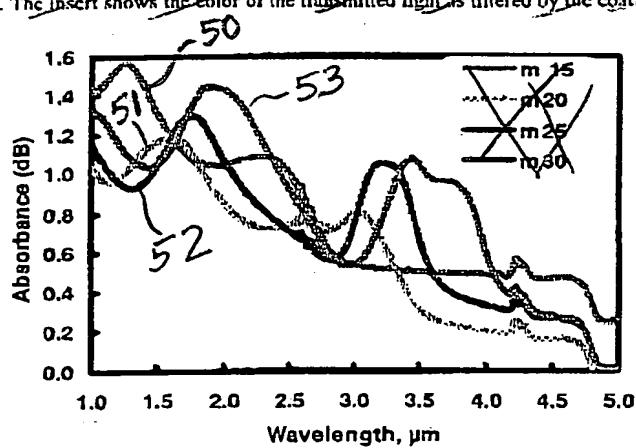


Fig. 3 FTIR spectra of 1,000- μm -bore Ag/PbS HGWs for different deposition times in minutes.

The thickness of the thin films was obtained by direct measurements using a FESEM. A photomicrograph taken with the FESEM for a typical cross-section of the thin film combination Ag/CdS/PbS is shown in Fig. 4. The CdS film appears darker than the PbS film because the in-lens detector produces a negative image of the secondary electron image. The thicknesses of the films shown in Fig. 4 are; Ag 154 nm , CdS $169 \pm 16 \text{ nm}$, PbS $82 \pm 6 \text{ nm}$. We do not see any degradation of the underlying film when the new film is deposited over it. That is, CdS and PbS do not react with each other during the deposition of successive layers. The film thickness measured from the FESEM micrographs of both single and multilayer dielectric film are summarized in Table 1. These results agree very well with the optical thickness measurement.

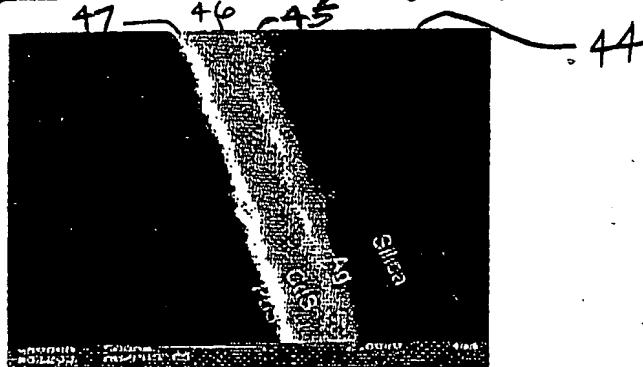


Fig. 4 Cross-sectional FESEM image of a 1.000- μm bore Ag/CdS/PbS HGW. The CdS and PbS thin films are deposited sequentially inside the Ag coated HGW.

Table 1 Thickness values for CdS and PbS thin films on Ag determined from FESEM Images

HGWs	Thickness of Ag nm	Thickness of CdS nm	Thickness of PbS nm
Ag/CdS	156 ± 16	172 ± 16	—
Ag/PbS	158 ± 20	—	96 ± 16
Ag/CdS/PbS	154	169	82 ± 6

A series of 1.000- μm bore HGWs with 1, 2, and 3 dielectric layers deposited over Ag were fabricated using wet chemistry methods [8, 11]. The spectral losses for these straight waveguides are shown in Fig. 5. From Fig. 5, it may be seen that the addition of each dielectric layer shifts the interference peaks to longer wavelengths. This is a result of the increase in thickness with each additional layer.

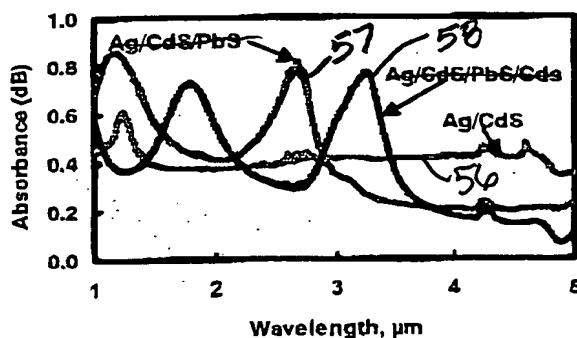
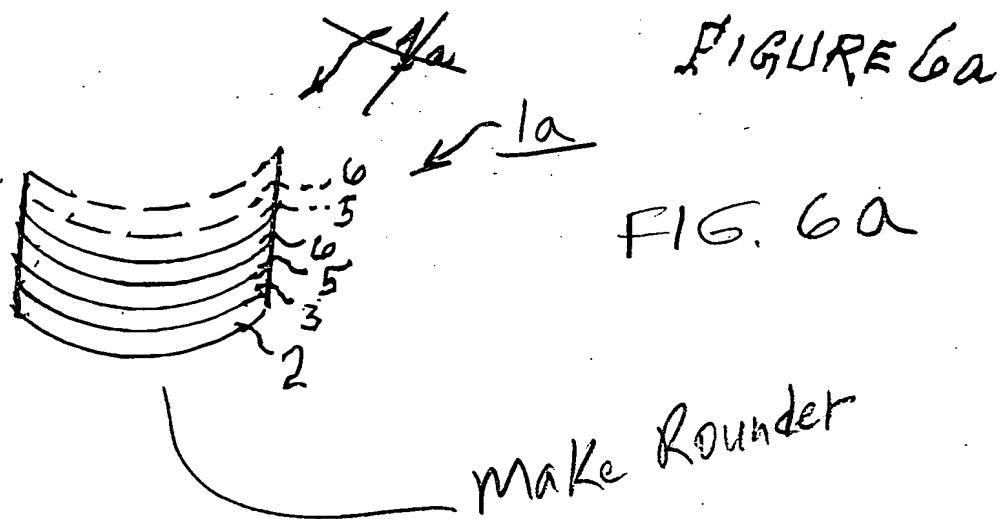
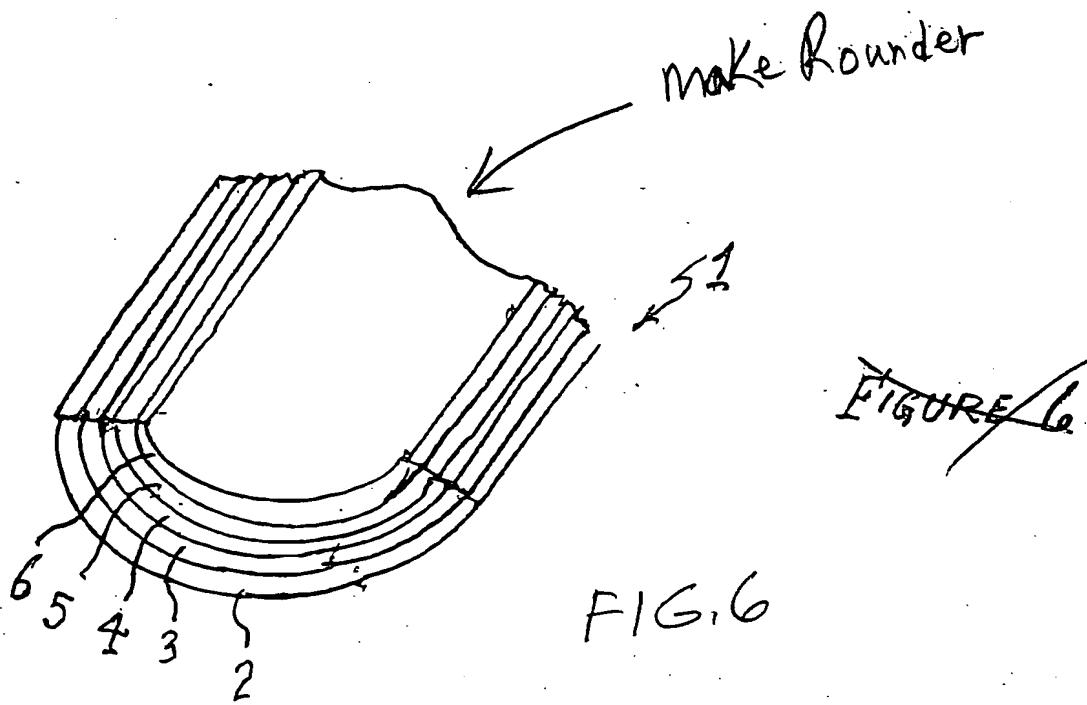


Fig. 5 FTIR Spectra of 1.000- μm bore of 1, 2, and 3-layer dielectric coatings on Ag coated HGWs. The spectra beyond 4 to 10 μm region are essentially flat and featureless.



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